

UNITED STATES PATENT APPLICATION

OF

Jeong Dae SEO, Kyung Hoon LEE,

Hee Jung KIM, Chun Gun PARK

and

Hyoung Yun OH

FOR

ORGANIC ELECTROLUMINESCENT DEVICE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of Korean Application Nos. P2002-83279 filed on December 24, 2002 and P2003-20465, filed on April 1, 2003, which are hereby incorporated by references as if fully set forth herein.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention relates to an organic luminescent device, and more particularly, to a blue emitting material of an emitting layer.

Description of the Related Art

[0003] Recently, with the trend of a large sized display, a request of a flat display that occupies a small area has been increased. One example of the flat display is an organic electroluminescent device also called as an organic light emitting diode (OLED). And, technology for the organic electroluminescent display is developed rapidly, whereby various prototypes have been in market already.

[0004] The organic electroluminescent device emits light in a manner that electric charges are injected in an organic layer formed between an anode and a cathode so as to form a pair of electron and hole to generate an exciton and an excited state of the exciton falls to a ground state so as to emit light.

[0005] The organic electroluminescent device is not only formed on a flexible transparent substrate such as a plastic but also operated at a lower voltage (less than 10V) compared to a plasma display panel or an inorganic electroluminescent display.

[0006] Also, the organic electroluminescent device has advantages in that power consumption is reduced and various colors are available.

[0007] Moreover, the organic electroluminescent device enables to express three colors including green, blue, and red. Therefore, many concerns are focused on the organic electroluminescent device as the next generation full color display.

[0008] The organic electroluminescent device may be realized to emit blue, green, or red light in accordance with a material forming the emitting layer.

[0009] Particularly, the emitting layer for blue luminescence is a host employing materials such as PBD and DPVBi and is fabricated by doping 1-3% of materials such as perylene, coumarine, and pyrene as a dopant.

[0010] However, it is a biggest problem in realizing blue luminescence of the organic electroluminescent device that a degree of color purity and the luminescence efficiency are lowered.

[0011] The conventional blue emitting materials emit light with a long wavelength during emission and had a problem of lowering the degree of color purity and the luminescence efficiency, and even more lowered at high doping density.

SUMMARY OF THE INVENTION

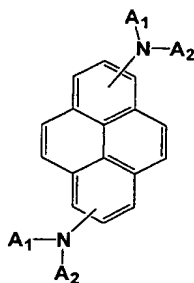
[0012] Accordingly, the present invention is directed to an organic electroluminescent device that substantially obviates one or more problems due to limitations and disadvantages of the related art.

[0013] An object of the present invention is to provide an organic electroluminescent device.

[0014] Additional advantages, objects, and features of the invention will be set forth in part in the description which follows and in part will become apparent to those having ordinary skill in the art upon examination of the following or may be learned from practice of the invention. The objectives and other advantages of the invention may be realized and attained by the structure particularly pointed out in the written description and claims hereof as well as the appended drawings.

[0015] To achieve these objects and other advantages and in accordance with the purpose of the invention, as embodied and broadly described herein, an organic luminescent device includes a substrate; a first and second electrodes formed on the substrate; an emitting layer formed between the first electrode and the second electrode, the emitting layer having a plurality of materials and being a blue emitting material using a chemical formula 1 as a dopant.

[0016] [Chemical formula 1]



In this case, at least one of A₁ and A₂ is selected from a substituted or non-substituted aromatic group, a heterocyclic group, an aliphatic group, and hydrogen.

[0017] Wt. % of the material in the chemical formula 1 is 0.1 - 49.9wt. % of a total weight of the emitting layer.

[0018] Material forming the emitting layer together with the material of the chemical formula 1 is formed as a structure of a following chemical formula 2.

[0019] [Chemical formula 2]



Wherein, the X is selected from a group consisting of naphthalene, anthracene, phenanthrene, pyrene, perylene, and quinoline and at least one of the B1 and B2 is selected from a group consisting of aryl, alkylaryl, alkoxyaryl, arylaminoaryl and alkylaminoaryl.

[0020] At least one of the B1, B2 is selected from phenyl, biphenyl, pyridyl, naphthyl, tritylphenyl, biphenylenyl, anthryl, phenanthryl, pyrenyl, perylenyl, quinolyl, isoquinolyl, fluorenyl, terphenyl, tolyl, xylyl, methylnaphthyl, and hydrogen.

[0021] At least one of the A1 and A2 is selected from a substituted or non-substituted phenyl, a substituted or non-substituted biphenyl, a substituted or non-substituted pyridyl, a

substituted or non-substituted naphthyl, a substituted or non-substituted quinolyl, a substituted or non-substituted isoquinolyl, a substituted or non-substituted fluorenyl, a substituted or non-substituted terphenyl, methyl, ethyl, propyl, i-propyl, and t-buthyl.

[0022] The substituent of each substituted A1 and A2 is at least one and selected from methyl, ethyl, propyl, i-propyl, t-butyl, cyclohexyl, methoxy, ethoxy, propoxy, butoxy, dimethylamino, trimethylsilyl, fluorine, choline, phenoxy, tolyloxy, dimethylamino, diethylamino, diphenylamino, and triphenylsilyl.

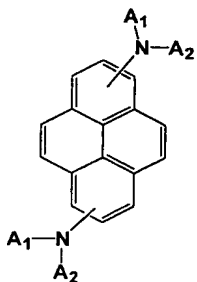
[0023] It is to be understood that both the foregoing general description and the following detailed description of the present invention are exemplary and explanatory and are intended to provide further explanation of the invention as claimed.

DETAILED DESCRIPTION OF THE INVENTION

[0024] Reference will now be made in detail to the preferred embodiments of the present invention, examples of which are illustrated in the accompanying drawings. Wherever possible, the same reference numbers will be used throughout the drawings to refer to the same or like parts.

[0025] In the present invention, the emitting layer formed between a first electrode and a second electrode includes a plurality of materials and a blue material using a following chemical formula as a dopant.

[0026] [Chemical formula 1]



[0027] In this case, at least one of A₁ and A₂ is selected from a substituted or non-substituted aromatic group, a heterocyclic group, an aliphatic group, or hydrogen.

[0028] A wt.% of the material in the chemical formula 1 is 0.1 ~ 49.9wt% among a total weight of the emitting layer. The material forming the emitting layer with the chemical formula 1 is formed as a structure of a following chemical formula 2.

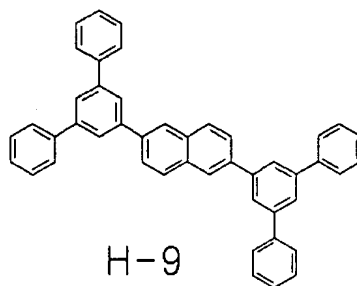
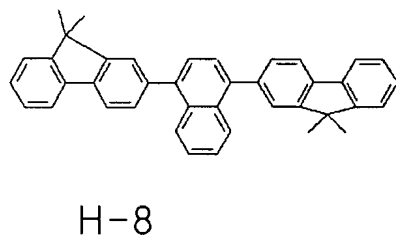
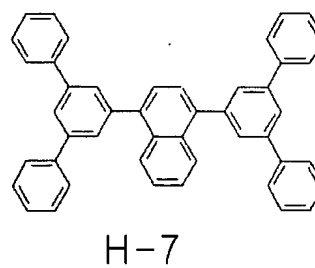
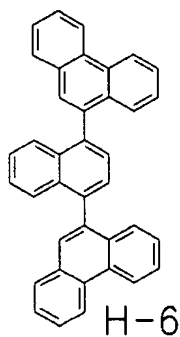
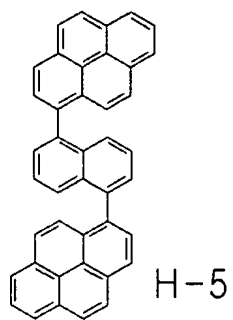
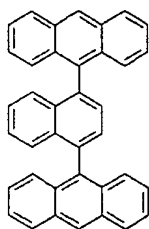
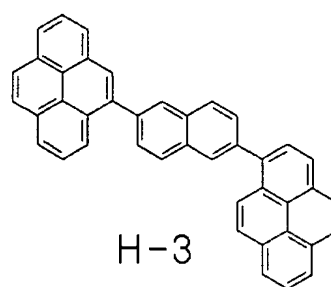
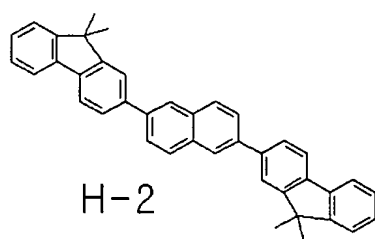
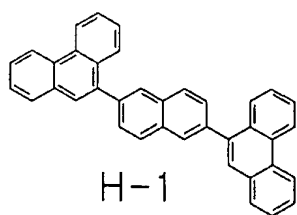
[0029] [Chemical formula 2]

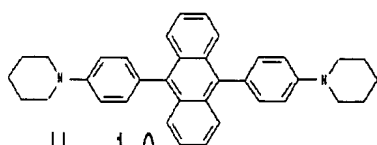
B1-X-B2

[0030] In this case, X is selected from a group consisting of naphthalene, anthracene, phenanthrene, pyrene, perylene, and quinoline. At least one of the B1 and B2 may be selected from a group consisting of aryl, alkylaryl, alkoxyaryl, arylaminoaryl and alkylaminoaryl.

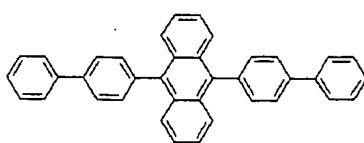
[0031] Also, at least one of the B1 and B2 may be selected from a group consisting of phenyl, biphenyl, pyridyl, naphthyl, tritylphenyl, biphenylenyl, anthryl, phenanthryl, pyrenyl, perylenyl, quinolyl, isoquinolyl, fluorenyl, terphenyl, tolyl, xylyl, methylnaphthyl, and hydrogen.

[0032] In this case, the material forming the emitting layer together with the chemical formula 1 is one of following chemical formulas.

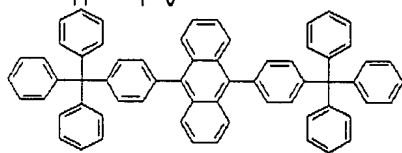




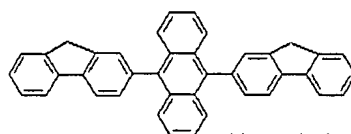
H - 10



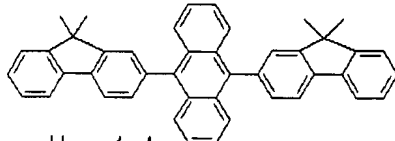
H - 11



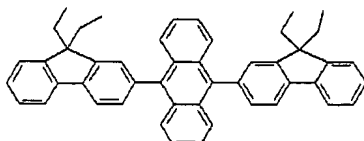
H - 12



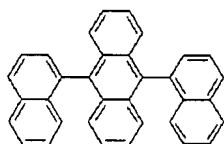
H - 13



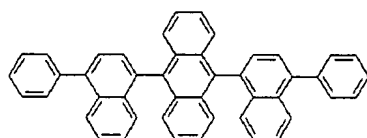
H - 14



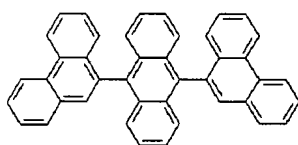
H - 15



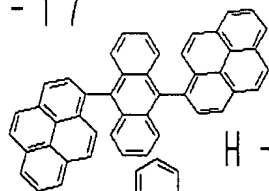
H - 16



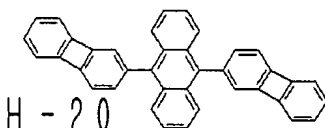
H - 17



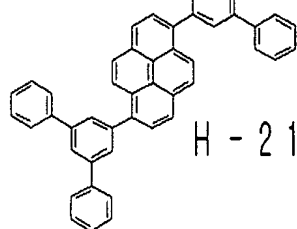
H - 18



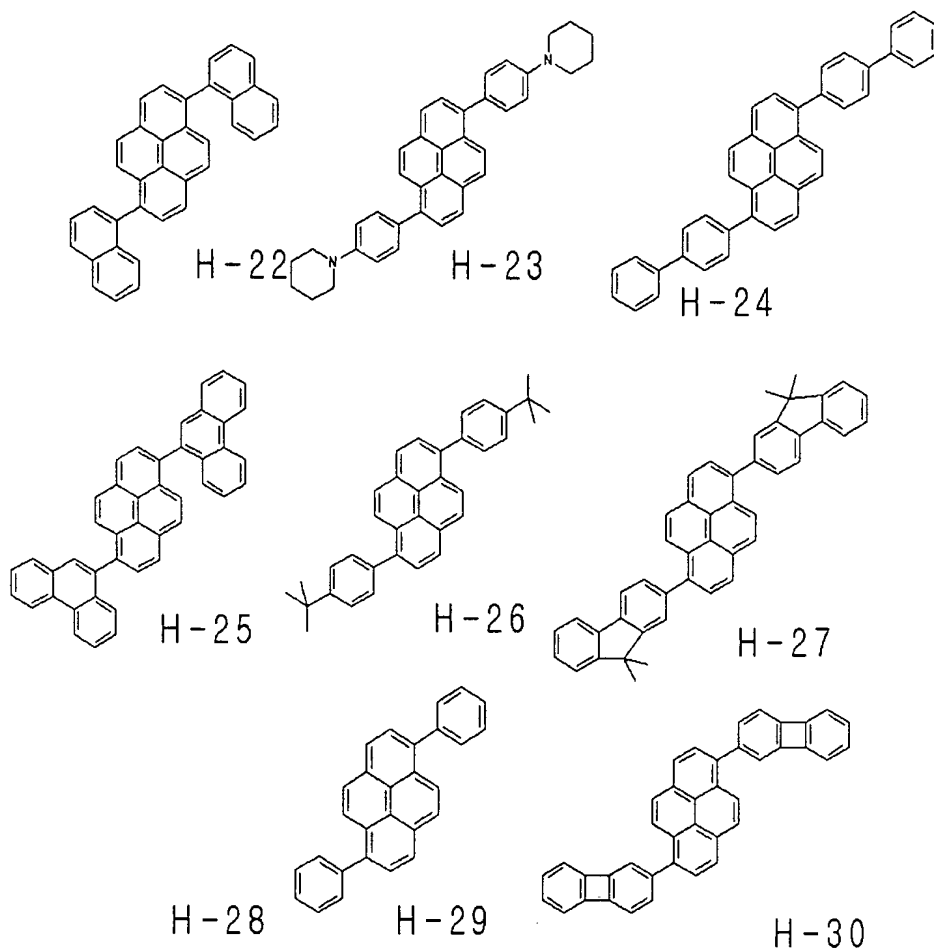
H - 19



H - 20



H - 21



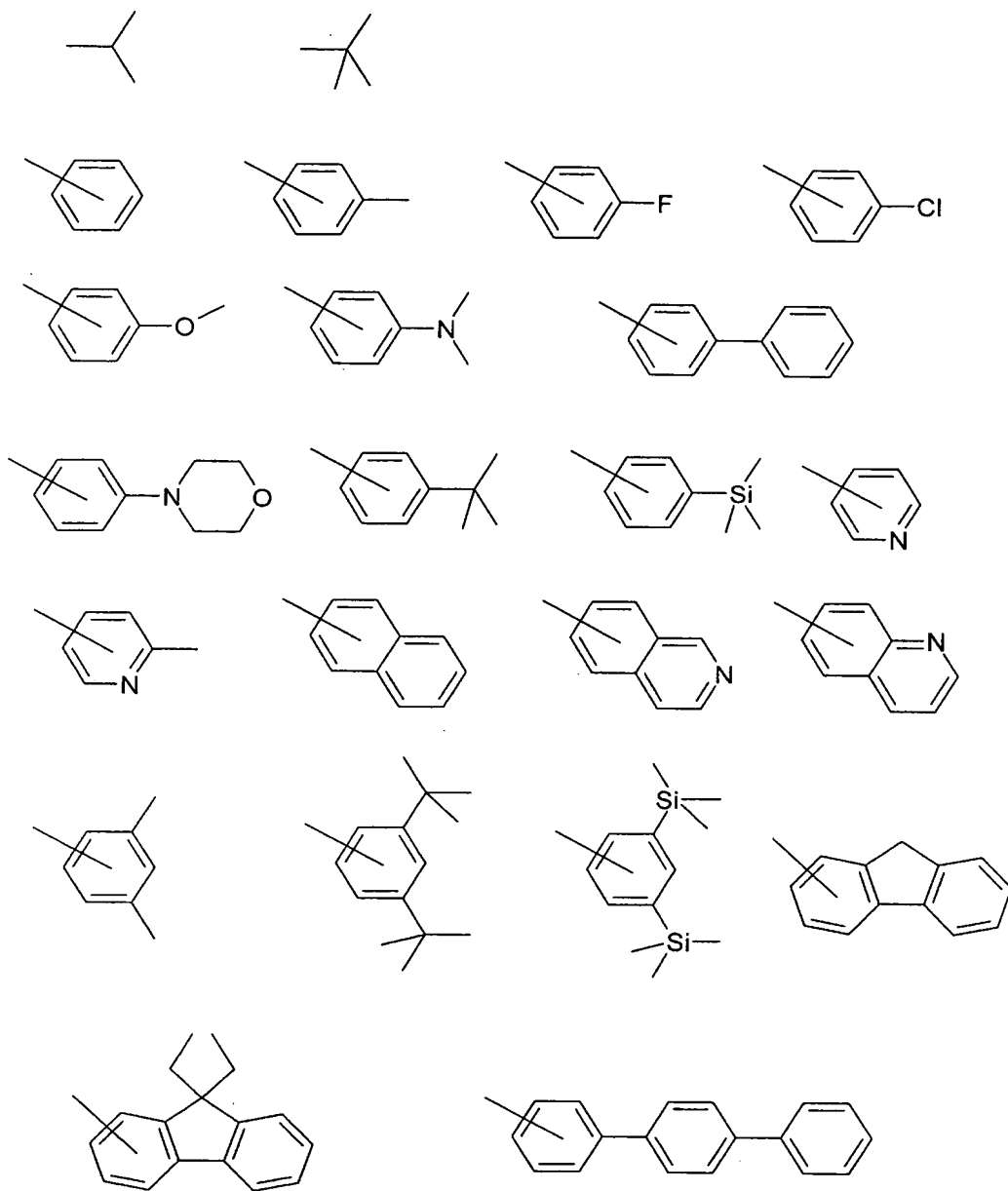
[0033] Also, in a case of the chemical formula 1, at least one of the A1 and A2 may be selected from a substituted or non-substituted aromatic group, a heterocyclic group, an aliphatic group, and hydrogen.

[0034] Particularly, at least one of A1 and A2 may be selected from a substituted or non-substituted phenyl, a substituted or non-substituted biphenyl, a substituted or non-substituted pyridyl, a substituted or non-substituted naphthyl, a substituted or non-substituted quinolyl, a substituted or non-substituted isoquinolyl, a substituted or non-substituted fluorenyl, a substituted or non-substituted terphenyl, methyl, ethyl, propyl, i-propyl, and t-buthyl.

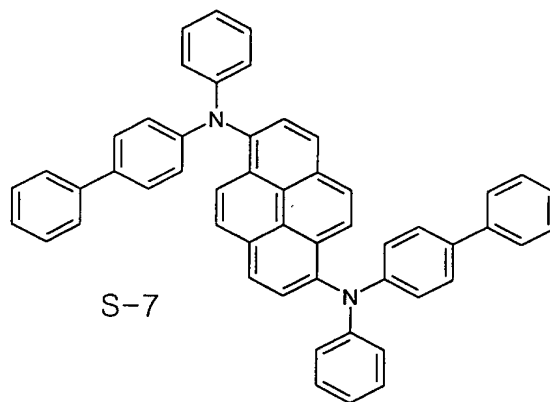
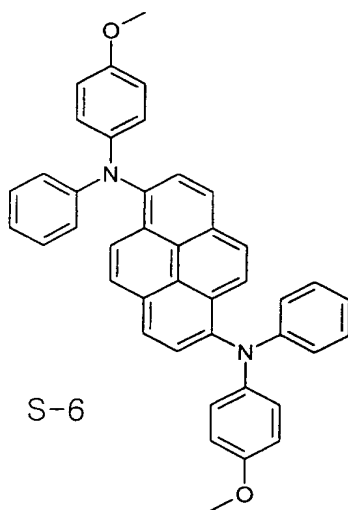
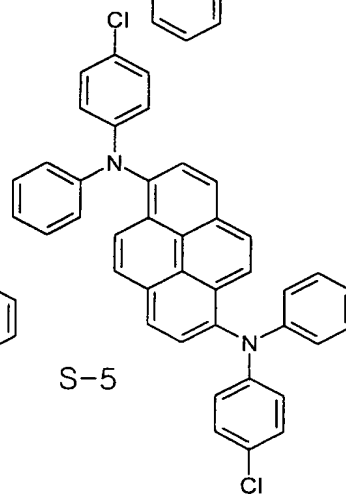
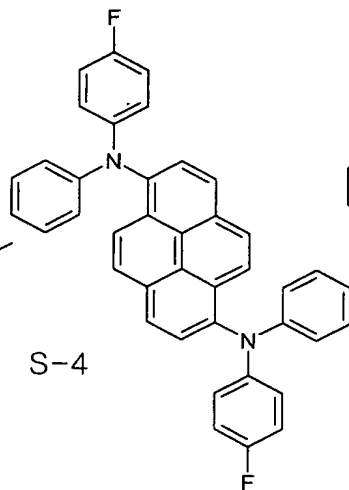
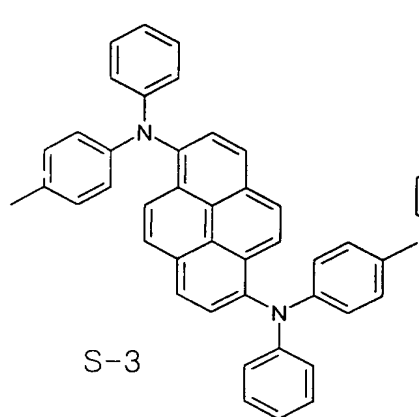
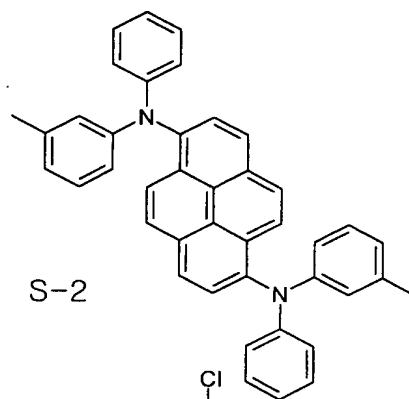
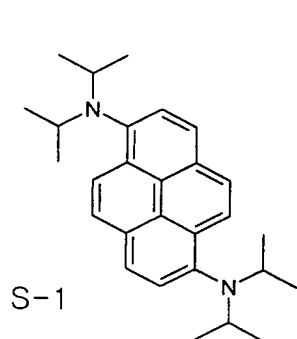
[0035] In this case, each substituent of the substituted A1 and A2 is at least one and selected from alkyl, alkoxy, alkylamino, alkylsilyl, halogen, aryl, aryloxy, arylamino, arylsilyl, and hydrogen.

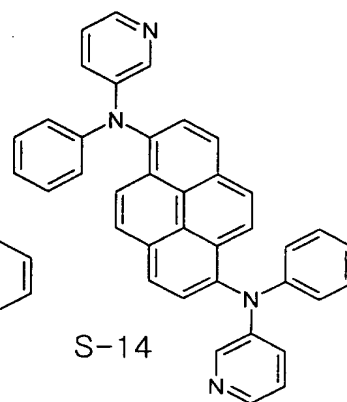
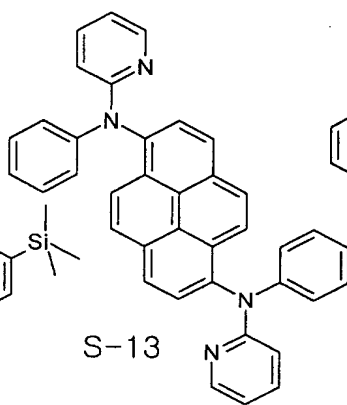
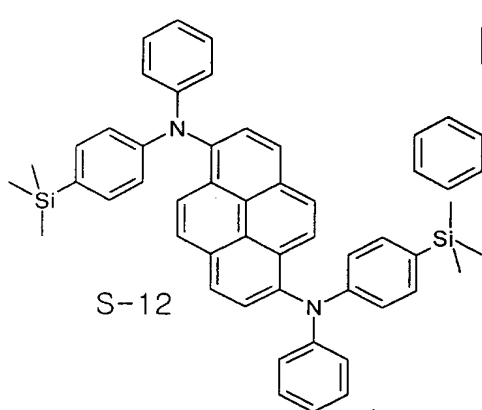
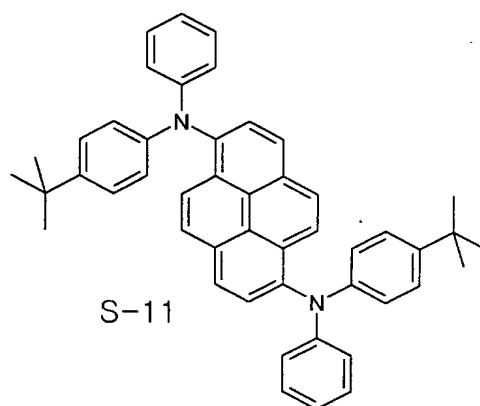
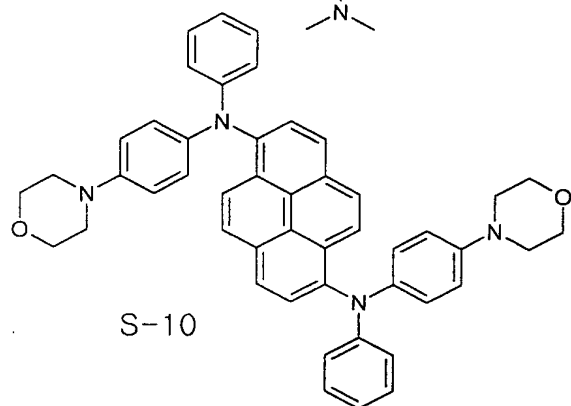
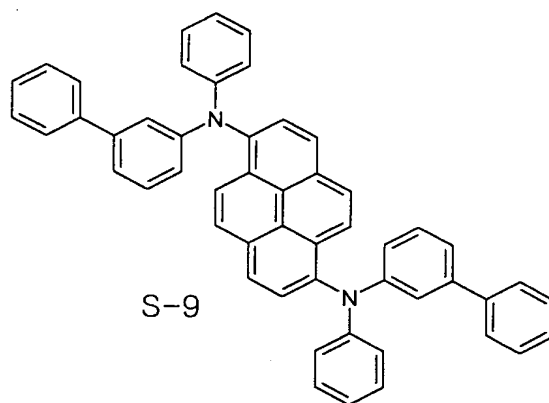
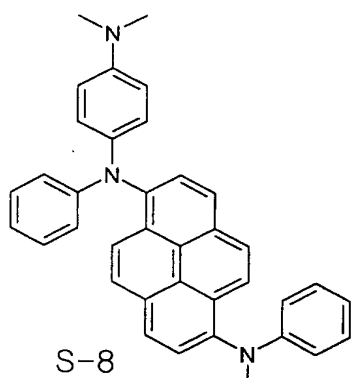
[0036] For example, the substituent of the A1 and A2 may be selected from methyl, ethyl, propyl, i-propyl, t-butyl, cyclohexyl, methoxy, ethoxy, propoxy, butoxy, dimethylamino, trimethylsilyl, fluorine, chlorine, phenoxy, tolyloxy, dimethylamino, diethylamino, diphenylamino, and triphenylsilyl.

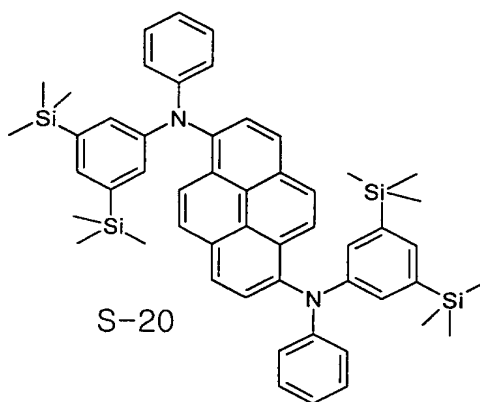
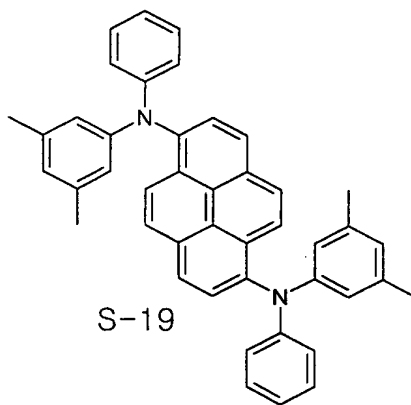
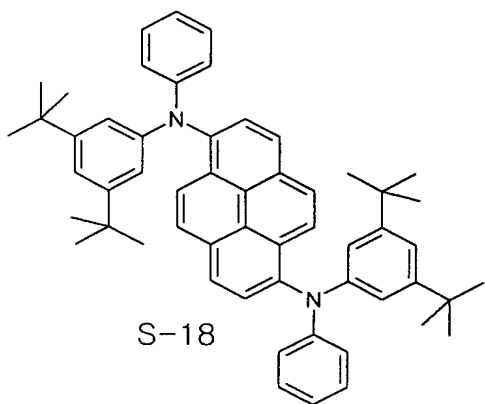
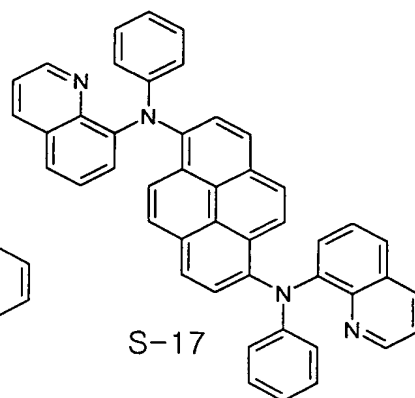
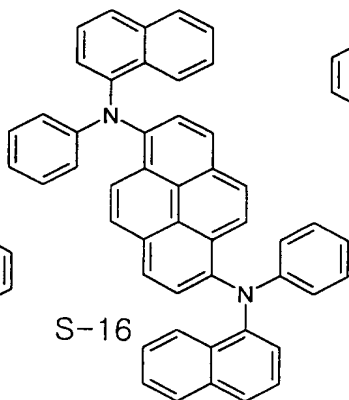
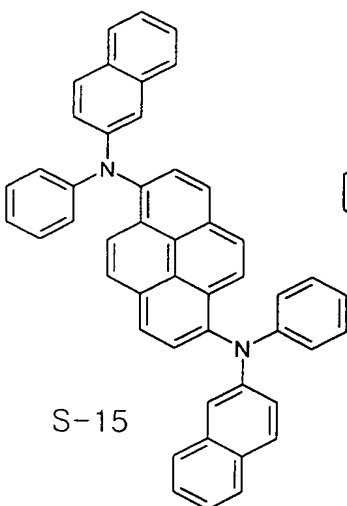
[0037] Particularly, at least one of the substituted or non-substituted A1 and A2 may be one of the following chemical formulas.

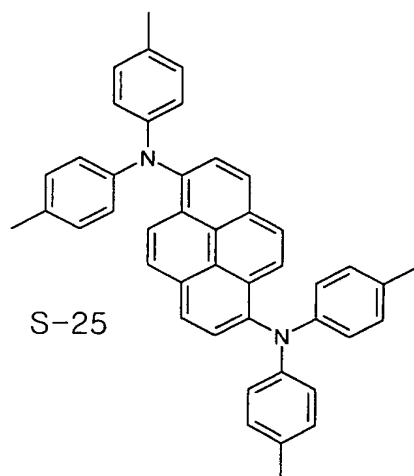
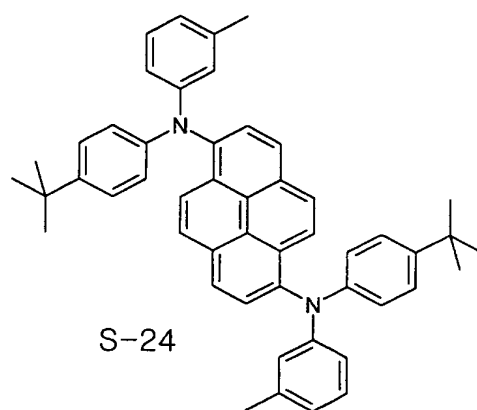
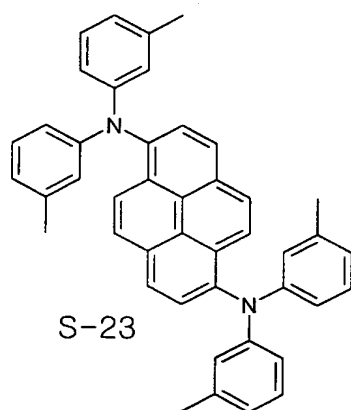
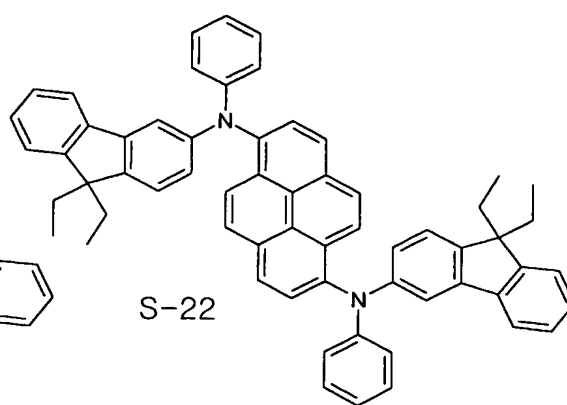
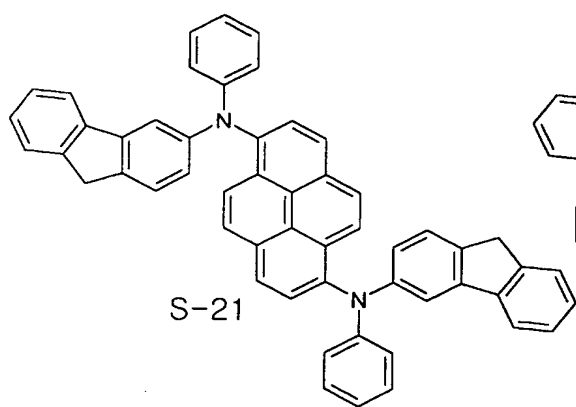


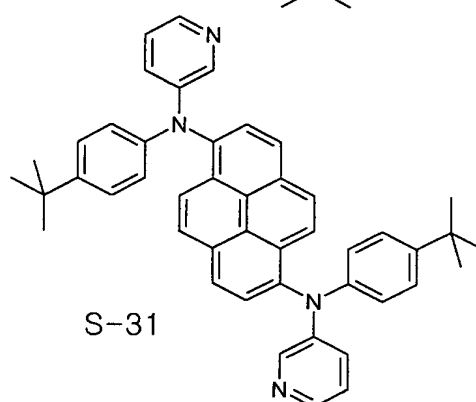
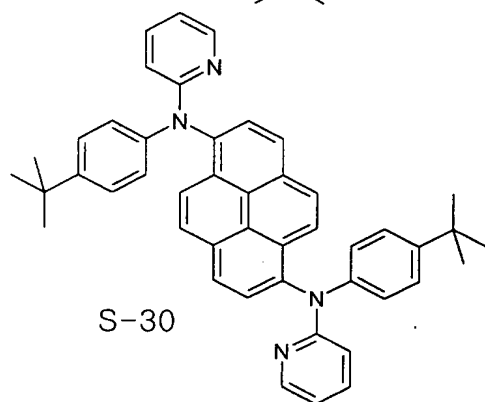
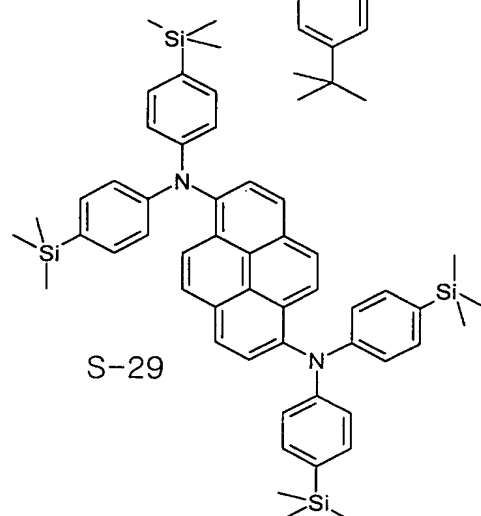
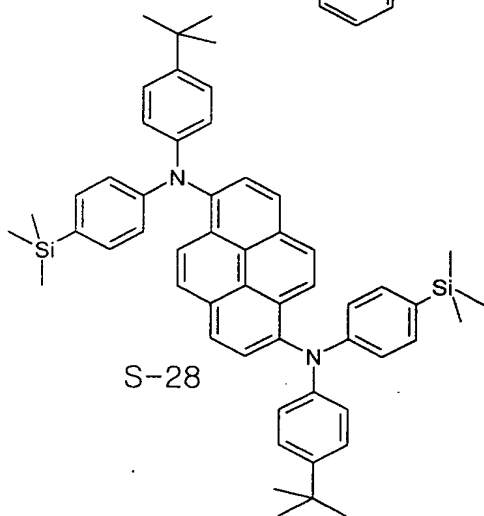
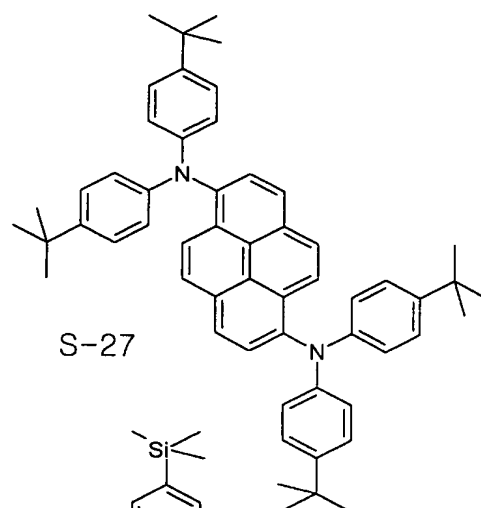
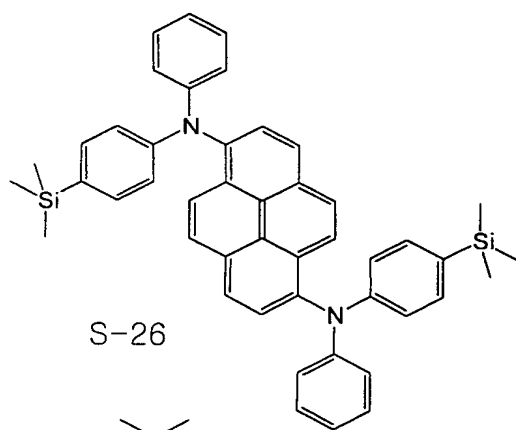
[0038] The blue emitting material having the substituent of the present invention may be one of the following chemical formulas.

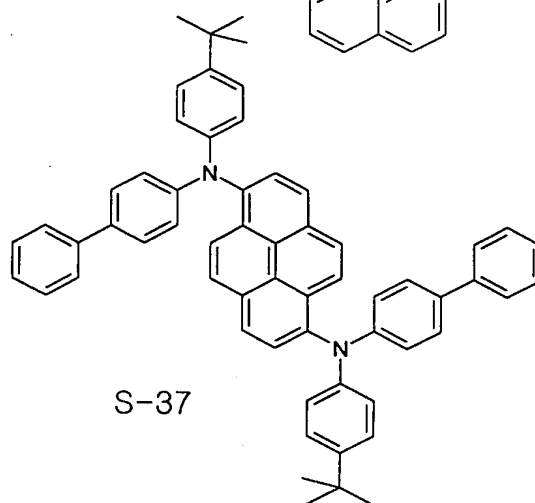
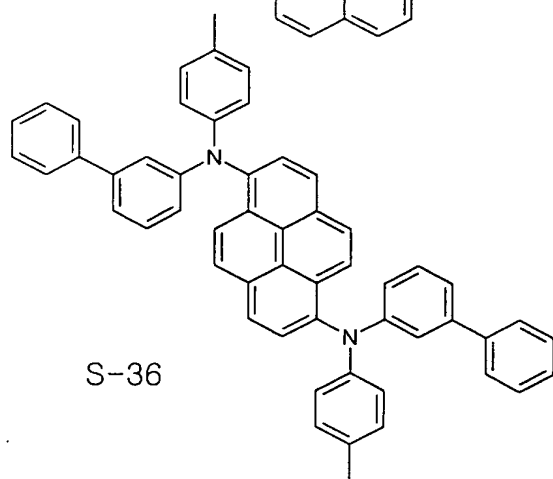
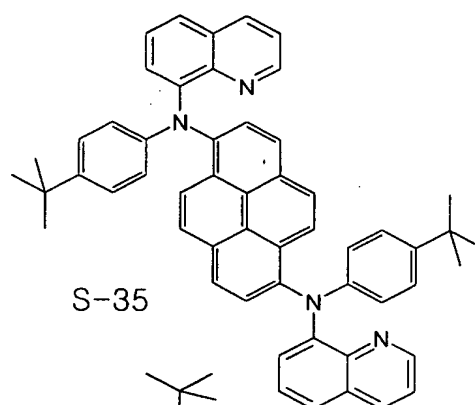
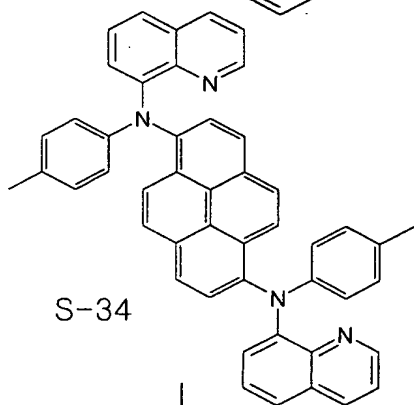
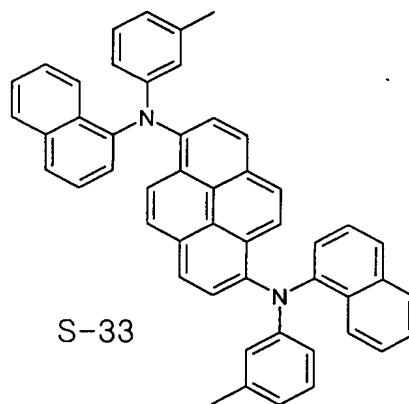
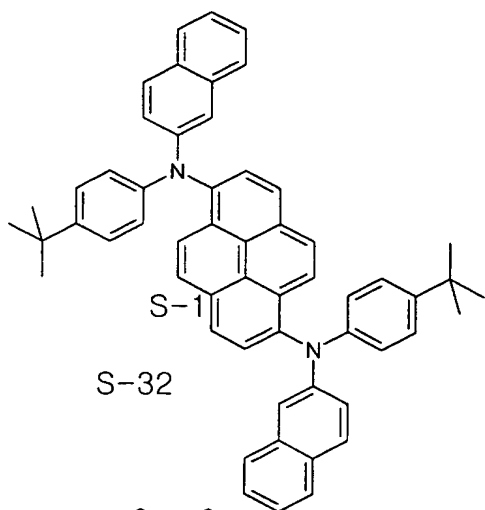


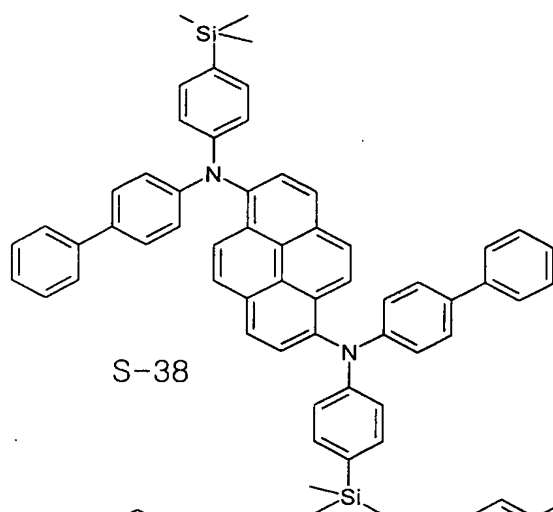




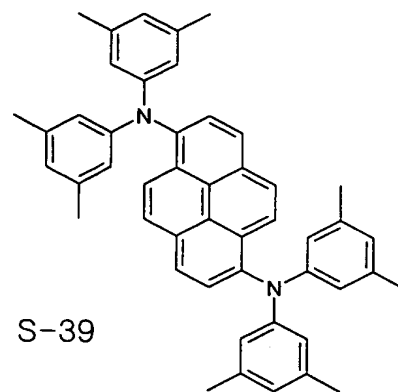




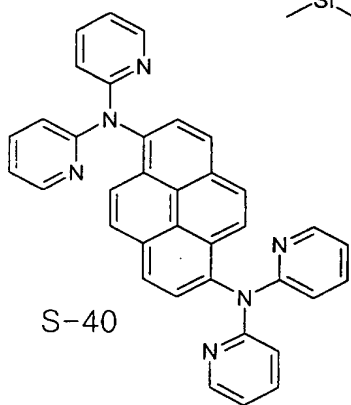




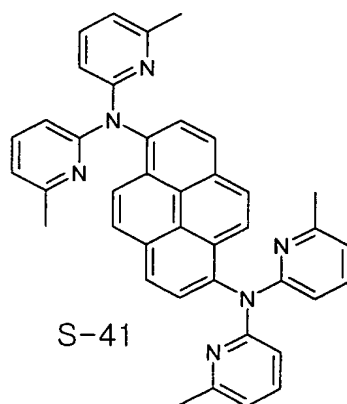
S-38



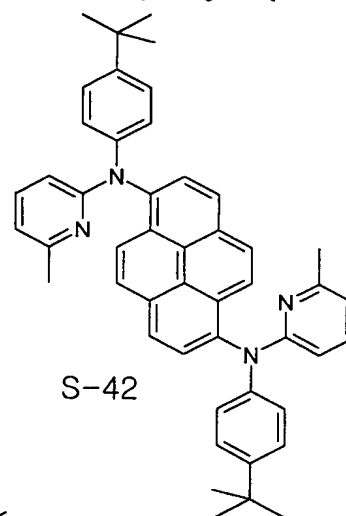
S-39



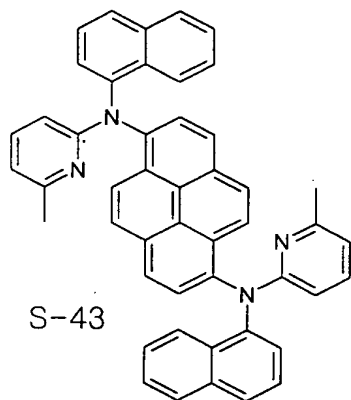
S-40



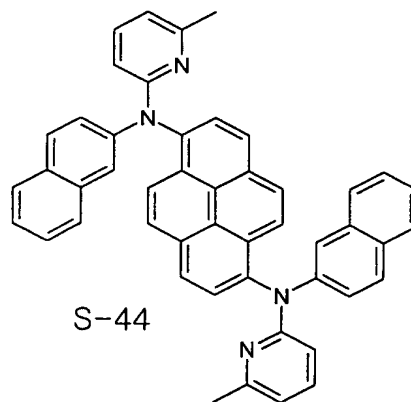
S-41



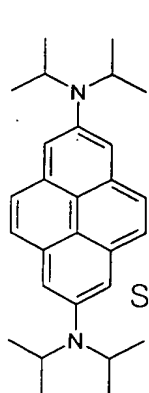
S-42



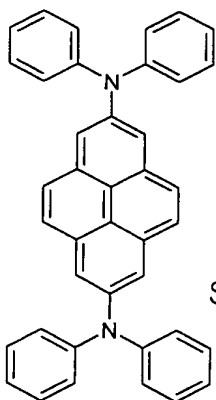
S-43



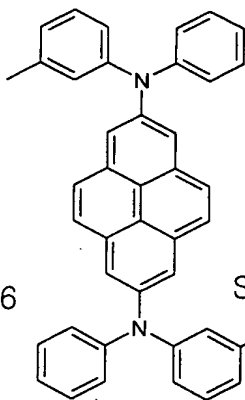
S-44



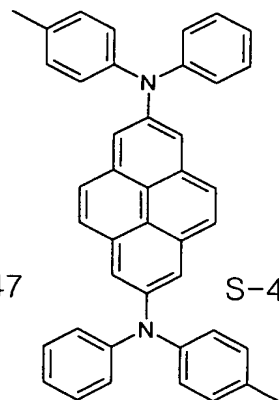
S-45



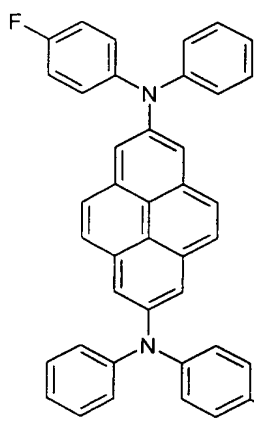
S-46



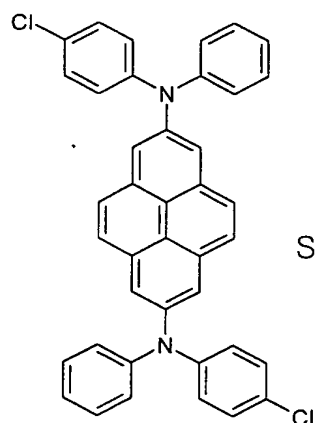
S-47



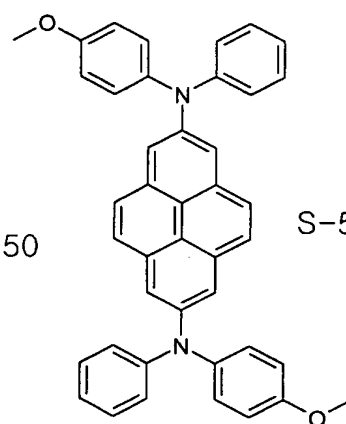
S-48



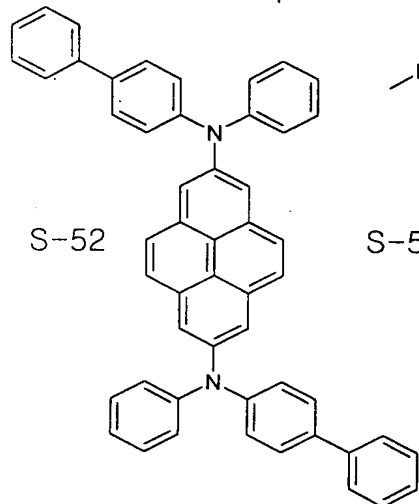
S-49



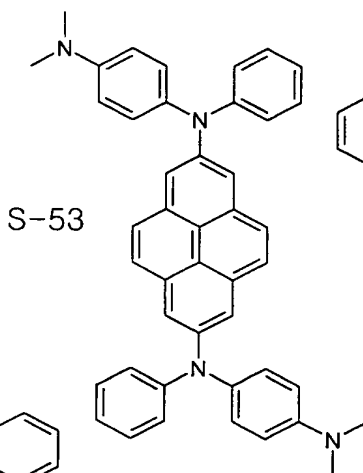
S-50



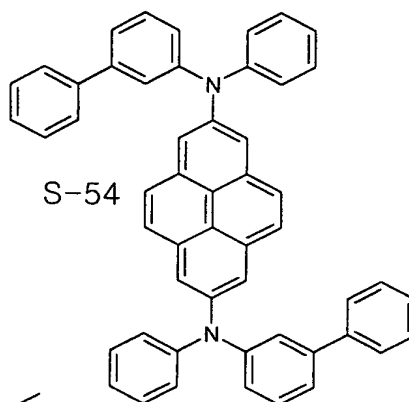
S-51



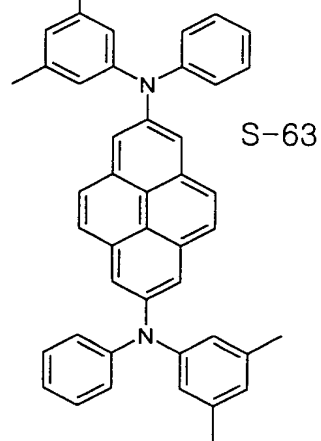
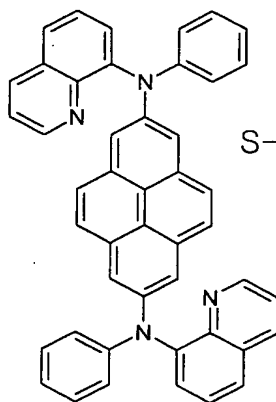
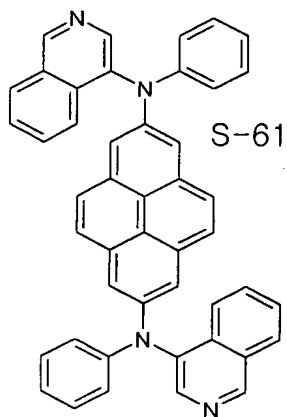
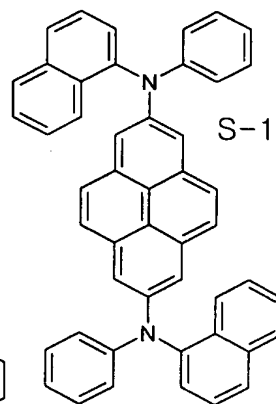
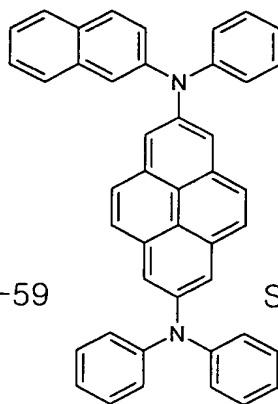
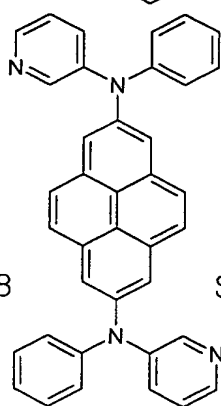
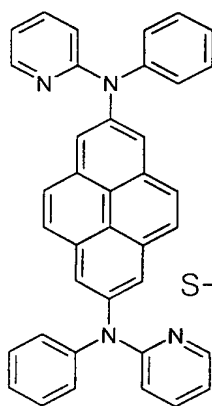
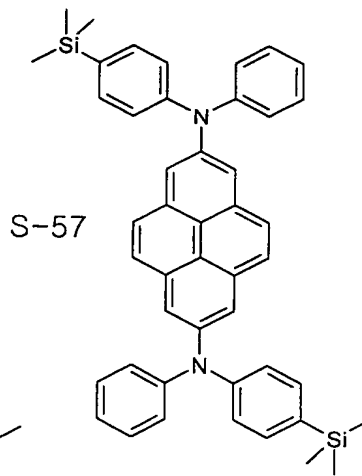
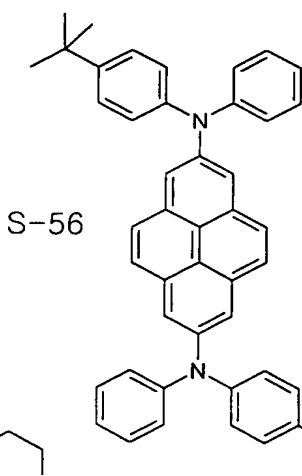
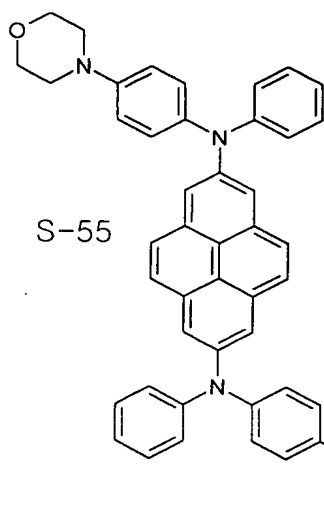
S-52

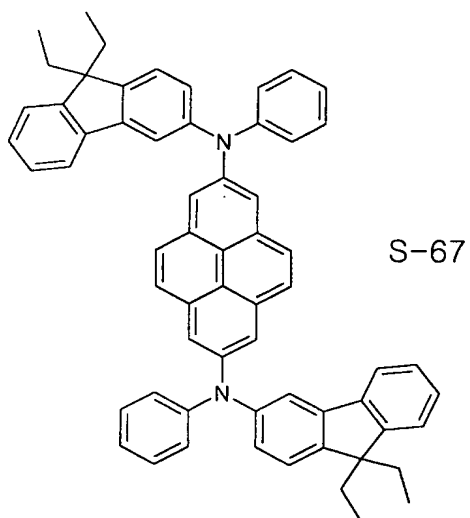
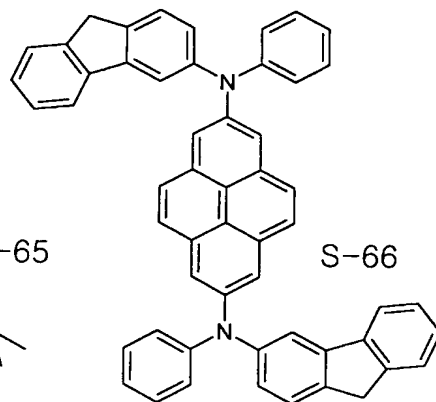
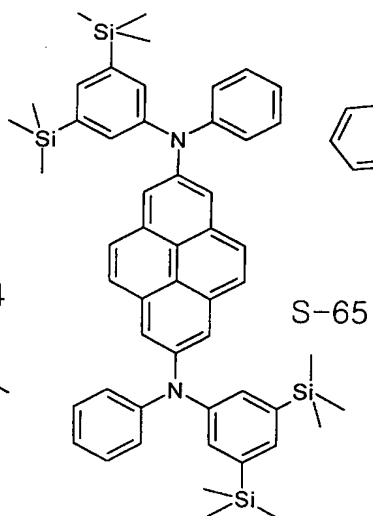
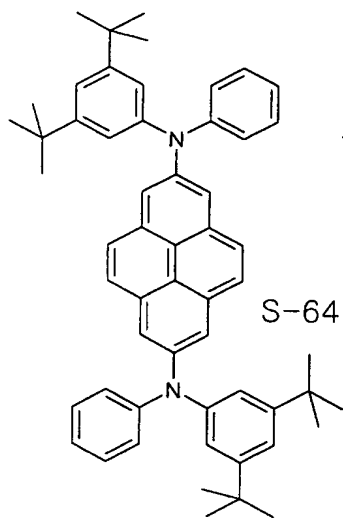


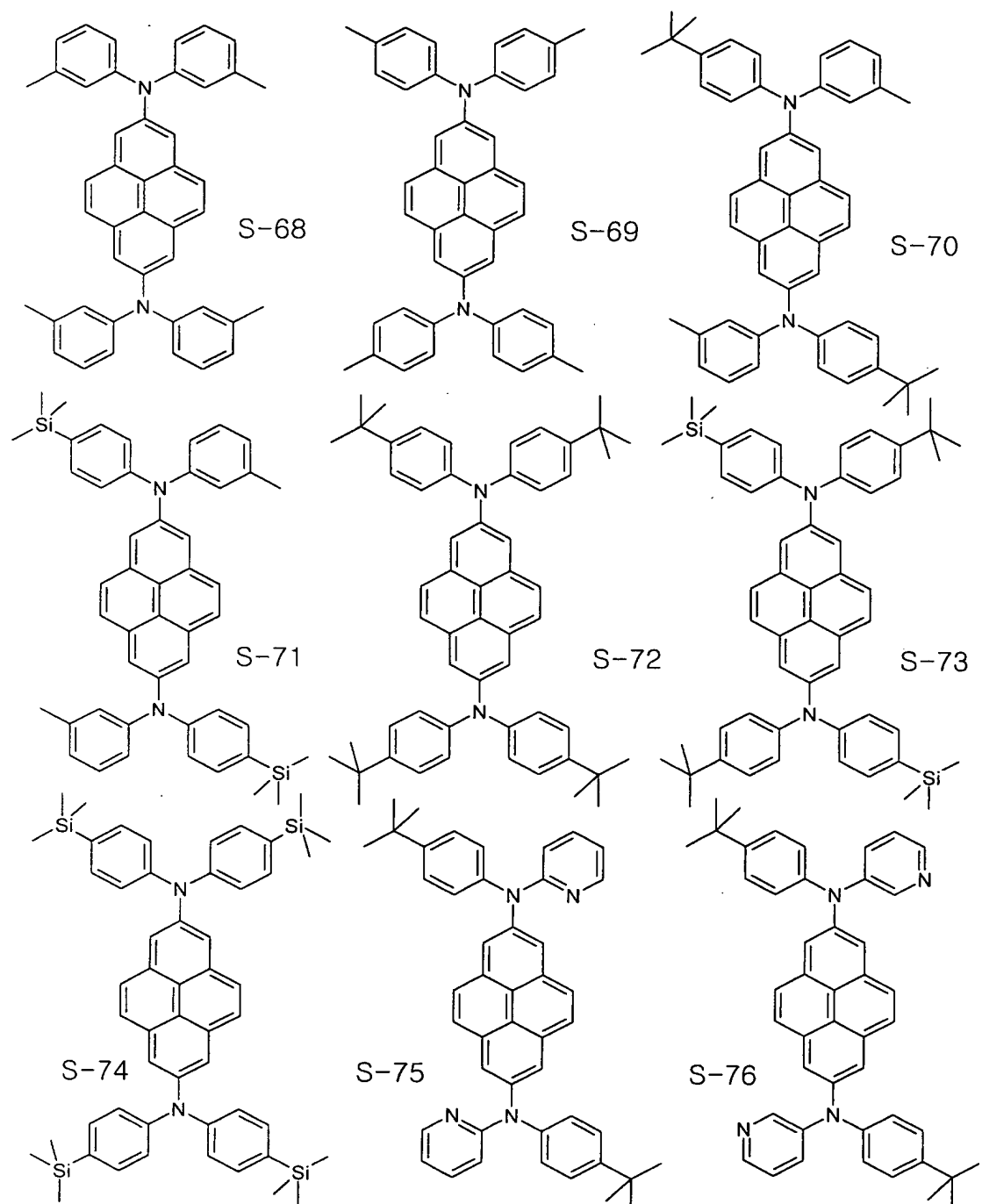
S-53

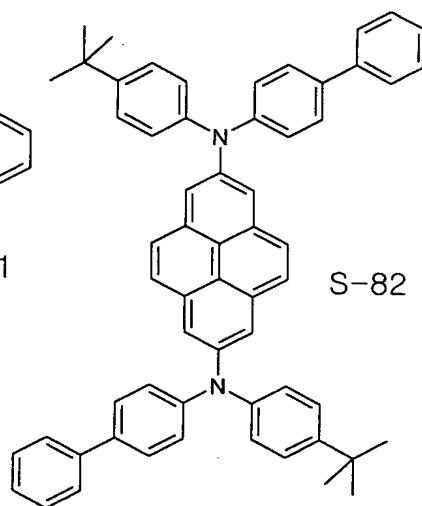
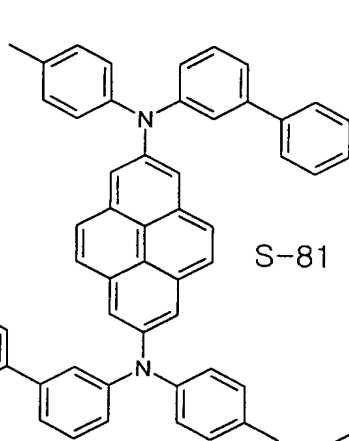
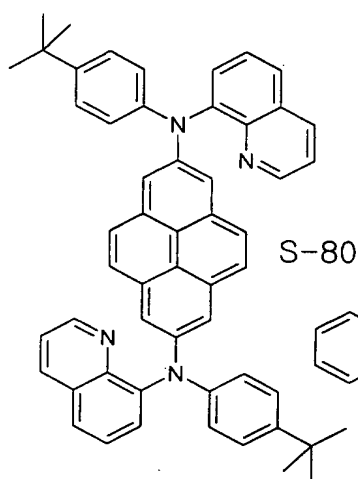
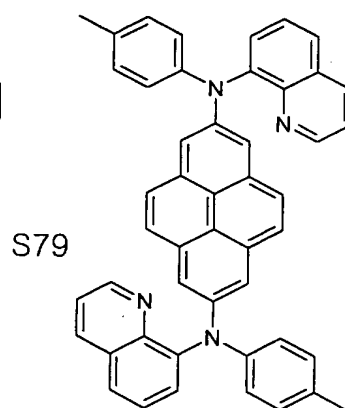
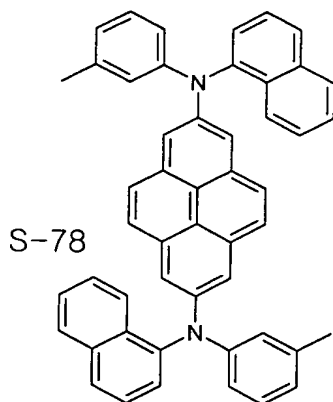
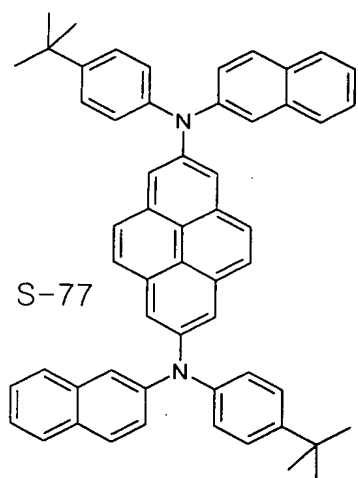


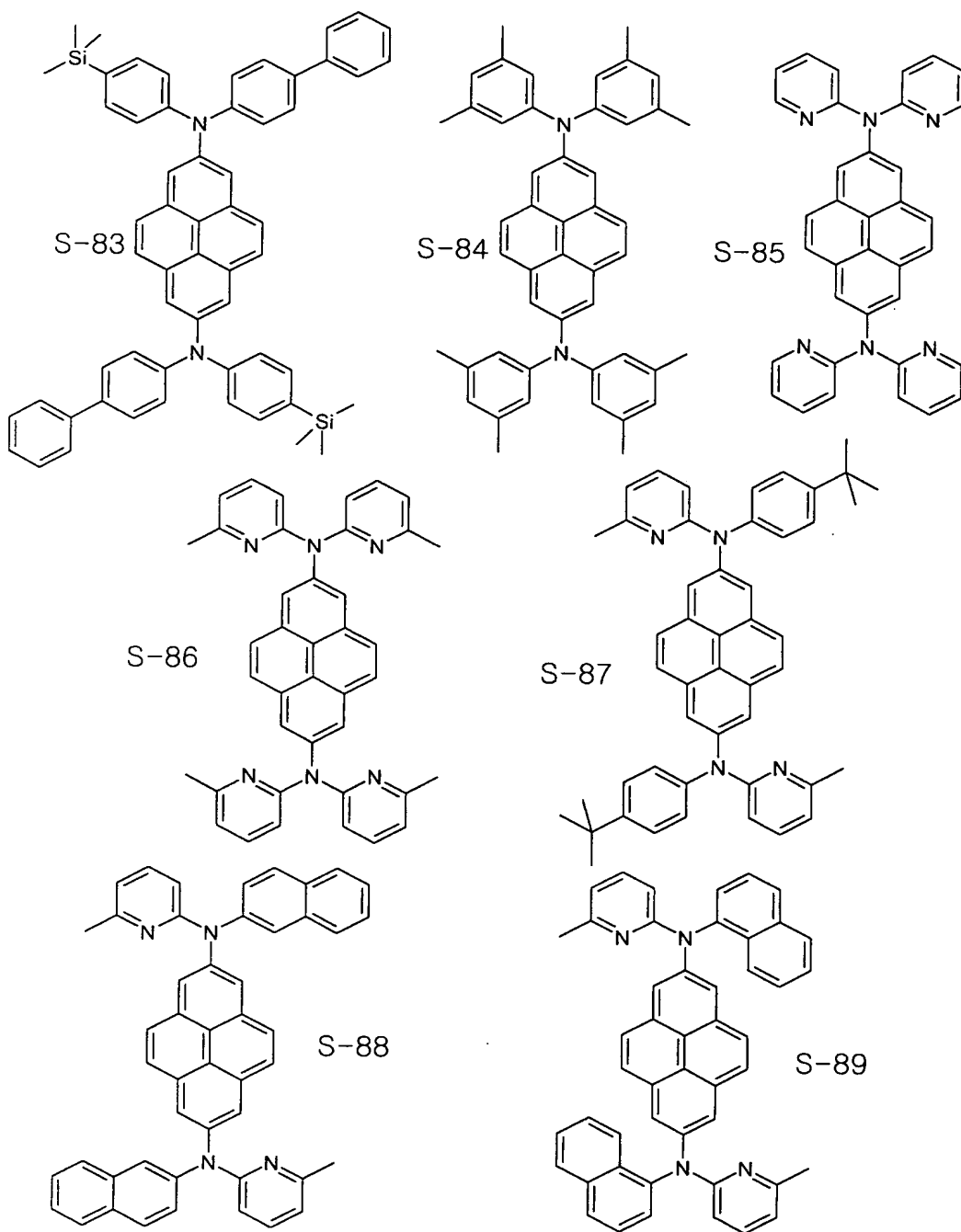
S-54





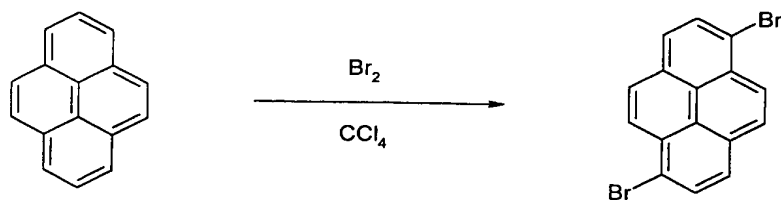






[0039] According to the organic electroluminescent device, N,N'-Bis-(4-tert-butyl-phenyl)-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine employed as the blue emitting material is compounded as follows.

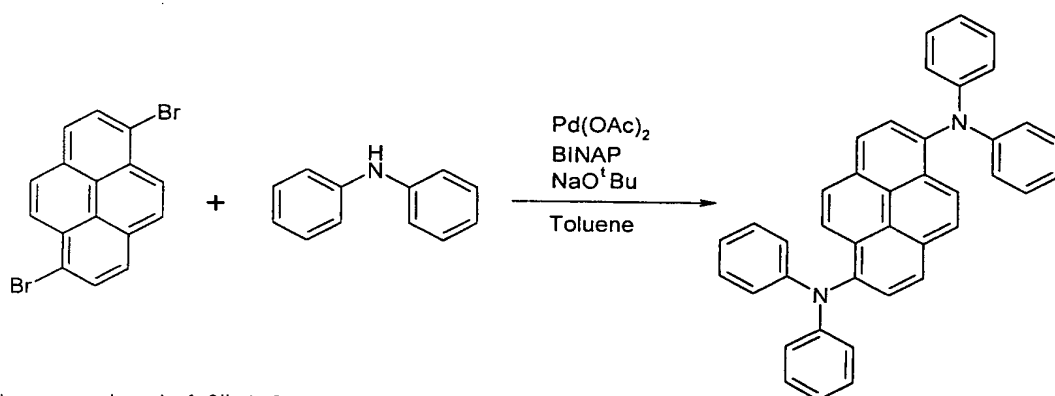
[0040] (1) Synthesis of 1,6-Dibromopyrene



[0041] First, pyrene (10g, 0.0049mol) is dissolved into CCl_4 (300mL) in a 3-necks-r.b.f. . And, Br_2 (17.38g, 0.108mol) and CCl_4 (50mL) are put into a dropping funnel provided at the round-floor flask and slowly dropped in the round-floor flask for 4 hours. N_2 is added to and HBr is removed from the solution. When the process is finished, the solution is stirred under N_2 current for one hour and formed sediment is filtered.

[0042] When the sediment is recrystallized by toluene, a green solid matter (6.05g, 34%) of 1,6-Dibromopyrene and a white solid matter of 1,8-Dibromopyrene (5g, 28%) are obtained.

[0043] (2) Synthesis of N,N,N',N'-Tetraphenyl-pyrene-1,6-diamine



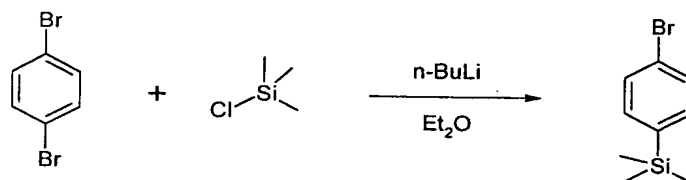
[0044] First, 1,6-Dibromopyrene(3g, 0.0083mol), Diphenylamine (4.23g, 0.025mol), BINAP([2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl])(0.052g, 1% mol), $\text{Pd}(\text{OAc})_2$ [Palladium(II)acetate](0.019g, 1% mol) and NaO^tBu [Sodium tert-butoxide](2.3g, 0.029mol) are dissolved into toluene (80mL) in 2-necks-r.b.f. so as to be refluxed.

[0045] When the reaction is finished, the 2-necks-r.b.f. is cooled at a normal temperature and about 40ml of toluene, that is, a reaction solvent is removed by distillation under reduced pressure.

[0046] When methanol (100ml) is added to the solution from which toluene 40ml is removed, sediment is generated.

[0047] When the sediment is filtered, a yellow solid matter of N,N,N',N'-Tetraphenylpyrene-1,6-diamine (3.22g, 72%) is obtained..

[0048] (3) Synthesis of (4-Bromo-phenyl)-trimethyl-silane



[0049] First, a dropping funnel is provided at the 3-necks-r.b.f. and the round-floor flask is dried under decompression. 1,4-Dibromobenzene (12,7g, 0.053mol) and the dried diethylether (300mL) are dissolved in the round-floor flask.

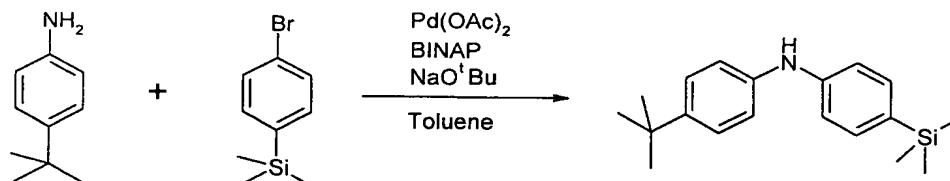
[0050] A dryice bath is provided at the round-floor flask, $n\text{-BuLi}$ (33,58mL, 0.0537mol) is put into the dropping funnel and $n\text{-BuLi}$ is slowly dropped, and a temperature is slowly raised from -78°C to 0°C .

[0051] Next, chloro trimethylsilane (7,51mL, 0.059mol) is slowly dropped at 0°C and then the temperature is raised again to the normal temperature for over a period of one hour.

[0052] When the reaction is finished, sediment is extracted by using diethylether and water is removed from the result by using MgSO_4 .

[0053] And then, after solvent is removed from the result, when the solvent is fractionally distilled under decompression, (4-Bromo-phenyl)-trimethyl-silane(11 ,3g, 92%) is obtained.

[0054] (4) Synthesis of (4-tert-Butyl-phenyl)-(4-trimethylsilanyl-phenyl)-amine

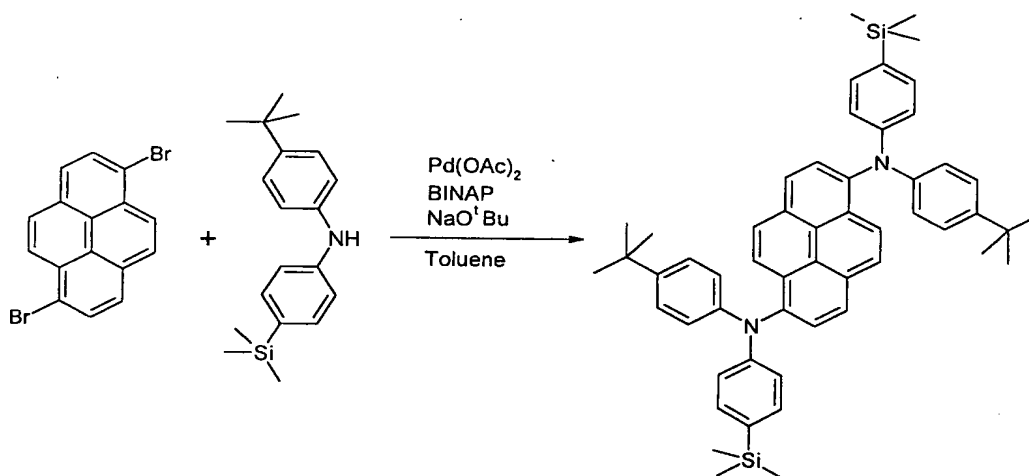


[0055] 4-tert-Butyl-phenylamine(1.2mL, 0.0076mol), (4-Bromo-phenyl)-trimethylsilane(1g,0.0044mol), BINAP(0.03g, 1%mol), Pd(OAc)₂(0.01g, 1%mol) and NaO^tBu(1.5g, 0.016mol) are dissolved into toluene(50mL) in the 2-necks-r.b.f. so as to be refluxed for about 2 hours.

[0056] When the reaction is finished, the 2-necks-r.b.f. is cooled and toluene, which is reaction solvent, is removed.

[0057] Next, when the sediment is filtered, the white solid matter such as (4-tert-Butyl-phenyl)-(4-trimethylsilanyl-phenyl)-amine (1.12g, 86%) is obtained.

[0058] (5) Synthesis of N,N'-Bis-(4-tert-butyl-phenyl)-N,N'-bis-(4-trimethylsilanyl-phenyl)-pyrene-1,6-diamine



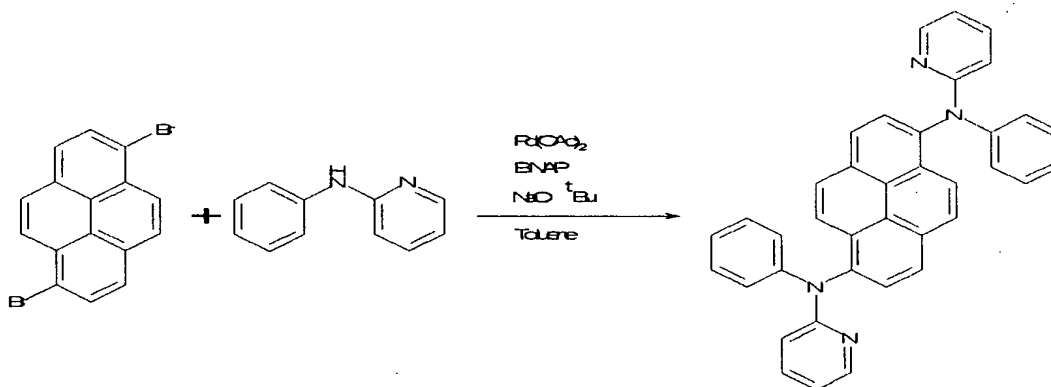
[0059] (1,6-Dibromopyrene)(0.787g, 0.0022mol), (4-tert-Butyl-phenyl)- (4-trimethylsilanyl-phenyl)-amine(1.56g, 0.00525mol), BINAP(0.054g, 4%mol), Pd(OAc)₂(0.015g, 3%mol) and NaO^tBu(0.93g, 0.0096mol) are dissolved in toluene (40mL) so as to be refluxed for 24 hours.

[0060] When reaction is finished, the round-floor flask is cooled and result material is extracted by using water and methylene chloride after toluene, that is, the reaction solvent is removed.

[0061] And then, water is removed from the result by using MgSO_4 and methylene chloride is removed by decompression, and silica gel chromatography is separated by using n-hexane : methylene chloride (6:1).

[0062] When the solvent is removed from the result and a solid matter is filtered by using nucleic acid, yellow solid matter such as (N,N'-Bis-(4-tert-butyl-phenyl)-N,N'-bis-(4-trimethylsilyl-phenyl)-pyrene-1,6-diamine)(1.09g, 63%) is obtained..

[0063] (6) Synthesis of N,N'-Diphenyl-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine

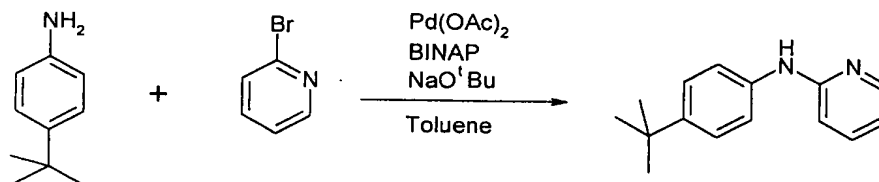


[0064] (1,6-Dibromopyrene) (1.2g, 0.0033mol), (Phenyl-pyridin-2-yl-amine)(1.36g, 0.008 mol), BINAP(0.083g, 4%mol), $\text{Pd}(\text{OAc})_2$ (0.022g, 3%mol) and NaO^tBu (1.28g, 0.013mol) are dissolved in toluene (50mL) in the 2-necks-r.b.f. so as to be refluxed for 24 hours.

[0065] When the reaction is finished, solid matter is generated.

[0066] When 50 % of toluene is removed from the solid matter, and methanol (70ml) is added to the solid matter, which then is filtered, yellow solid matter (N,N'-Diphenyl-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine)(0.81g, 45%) is obtained.

[0067] (7) Synthesis of (4-terr-Butyl-phenyl)-pyridin-2-yl-amine

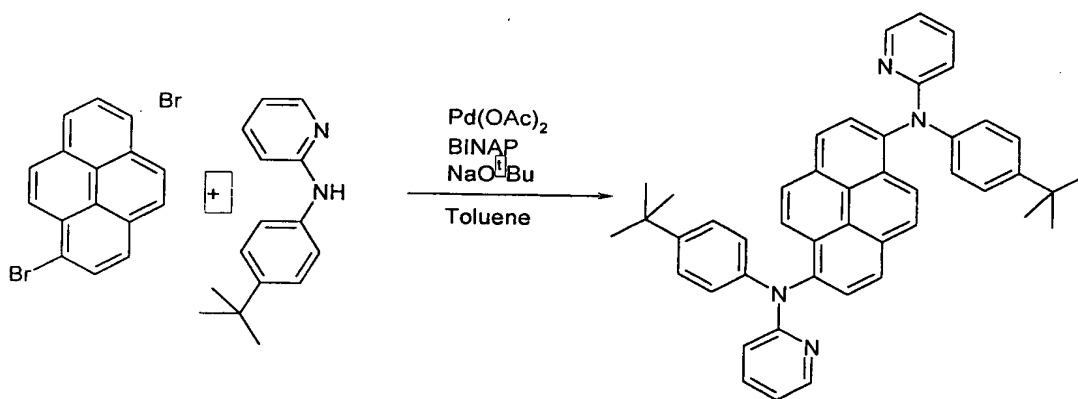


[0068] (4-tert-Butyl-phenylamine) (1.2mL, 0.0076mol), (2-Bromo pyridine)(1mL, 0.01mol), BINAP (0.06g, 4%mol), Pd(OAc)₂(0.02g, 3%mol) and NaO^tBu(1.5g, 0.016mol) are dissolved in toluene (50mL) in the 2-necks-r.b.f. so as to be refluxed for 24 hours.

[0069] When the reaction is finished, the 2-necks-r.b.f. is cooled and toluene, that is, reaction solvent is removed. Result material is extracted by using water and methylene chloride. methylene chloride is removed under decompression after water is removed by using MgSO₄.

[0070] Silica gel short column is generated by methylene chloride, sediment is formed by using nucleic acid. When the sediment is filtered, white solid matter such as 4-tert-Butyl-phenyl-pyridin-2-yl-amine (1.32g, 73%) is obtained.

[0071] (8) Synthesis of N,N'-Bis-(4-tert-butyl-phenyl)-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine



[0072] 1,6-Dibromopyrene(1g, 0.0028mol), (4-tert-Butyl-phenyl)-pyridin-2-yl-amine(1.51g, 0.0067mol), BINAP(0.07g, 4%mol), Pd(OAc)₂(0.02g, 3%mol)와 NaO^tBu(1.18g, 0.012mol) are dissolved in toluene (45mL) in the 2-necks-r.b.f. so as to be refluxed for 24 hours.

[0073] When the reaction is finished, solid matter is generated. 50% of toluene is removed from the solid matter, which is then filtered after methanol (70mL) is added thereto. When the solvent is removed by silica gel short column by using methylene chloride, (N,N'-Bis-(4-tert-butyl-Phenyl)-N,N'-di-pyridin-2-yl-pyrene-1,6-diamine)(0.99g, 60%) is obtained.

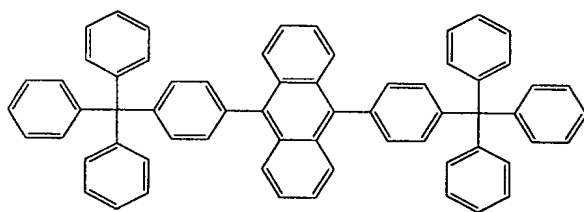
[0074] Hereinafter, a preferred embodiment of the organic electroluminescent device will be described according to the present invention.

[0075] [Embodiment]

[0076] An ITO glass is patterned so as to have a size of 3mm x 3mm. The patterned ITO glass is then cleaned.

[0077] A substrate is loaded on a vacuum chamber of which basic pressure is set up as 1×10^{-6} torr, CuPC(200 Å), NPB(500 Å), a light-emitting layer (300 Å), Alq₃(500 Å), LiF(5 Å), and Al(1,000 Å) are deposited on the ITO in order.

[0078] In this case, material in a following drawing is employed as a first HOST of the emitting layer and a mixing ratio of the host and dopant is 1:0.01.



HOST-1

[0079] [First embodiment]

[0080] When about 1mA of electric current is flown by using dopant having a chemical formula of S-26, brightness shows about 3.2cd/A, whereby CIE (Commision Internationale de L'Eclairage) $x=0.146$, $y=0.205$.

[0081] [Second embodiment]

[0082] When about 1mA of electric current is flown by using dopant having a chemical formula of S-28, brightness shows about 3.4cd/A, whereby CIE (Commision Internationale de L'Eclairage) $x=0.15$, $y=0.196$.

[0083] [Comparative embodiment]

[0084] ITO (Indium Tin Oxide) glass is patterned so as to have a size of 3mm x 3mm. The patterned ITO glass is then cleaned.

[0085] A substrate is loaded on a vacuum chamber of which basic pressure is set up as 1×10^{-6} torr, and such an organic matters as CuPC(200 Å), NPB(500 Å), emitting layer (300 Å), Alq₃(200 Å), LiF(5 Å), and Al(1000 Å) are deposited on the ITO glass.

[0086] When about 1mA of electric current is flown, brightness is about 1.8cd/A, whereby CIE (Commision Internationale de L'Eclairage) $x=0.15$, $y=0.196$.

[0087] Accordingly, the present invention is a blue emitting material of an emitting layer and an organic elecroluminescent device with blue color purity and a high luminescent efficiency is obtained by material with high color purity.

[0088] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the spirit or scope of the inventions. Thus, it is intended that the present invention covers the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.